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# Intensification of heat transfer during spinodal decomposition of a superheated aqueous oligomer solution

D V Volosnikov<sup>1</sup>, I I Povolotskiy<sup>1</sup>, A A Igolnikov<sup>1</sup>, M G Vasin<sup>2,4</sup>,  
L D Son<sup>3,4</sup> and P V Skripov<sup>1</sup>

<sup>1</sup> Institute of Thermal Physics of the Ural Branch of the Russian Academy of Sciences, Amundsen Street 107a, Ekaterinburg 620016, Russia

<sup>2</sup> Institute for High Pressure Physics of the Russian Academy of Sciences, Kaluzhskoe Shosse 14, Troitsk, Moscow 142190, Russia

<sup>3</sup> Ural State Pedagogical University, Kosmonavtov Avenue 26, Ekaterinburg 620017, Russia

<sup>4</sup> Ural Federal University, Lenina Avenue 51, Ekaterinburg 620000, Russia

E-mail: [dima\\_volosnikov@mail.ru](mailto:dima_volosnikov@mail.ru)

**Abstract.** The heat conduction of an aqueous solution of polypropylene glycol in the region of stable and unstable states was studied by the method of pulse isothermal impact on a substance with a characteristic time of 100 ms. It has been shown that the short-term superheating of a homogeneous solution not only above the liquid–liquid equilibrium temperature (low critical solution temperature), but also above the diffusion spinodal is fundamentally possible. The negative character of the deviation of the heat conduction of a solution from the additive law calculated from the heat conduction of the pure components at a given temperature was revealed. The signs of manifestation of spinodal decomposition accompanied by a significant intensification of heat transfer were found.

## 1. Introduction

The relevance of studying heat transfer in an aqueous solution of polypropylene glycol, a typical solution with low critical solution temperature (LCST), is dictated by both research and practical interest. Chemical technologies based on polypropylene glycols and water involve the stages of thermal load, including intense short-term heating under conditions of changing concentration and pressure. For practice, it is important to know the phase diagram of the solution, first of all, the liquid–liquid equilibrium line and the liquid–vapor critical curve [1–3]. Moreover, diffusion and heat transfer processes during pulse heating outside the temperature region of the homogeneous existence of a solution often remain unexplored. The reason is the difficulties in performing reliable measurements and systematic studies associated with the inability to use traditional quasi-static methods for investigation of fast processes.

The research interest of this work is to elucidate the features of heat transfer in solution under conditions of superposition of various factors. In particular, we are talking about reducing the heat conduction of the solution relative to the additive values for pure components [4] and intensifying heat transfer under conditions of pulse superheating against the background of the onset of the phase separation of the partially-soluble solution by the liquid–liquid mechanism and



the subsequent transition from the conductive to the mainly convective heat transfer mode. For such solutions, a heat transfer enhancement capacity has been revealed. This effect manifests itself at the diffusion spinodal intersection in the course of rapid heating of a solution in the case of LCST or its cooling in the case of so-called UCST (upper critical solution temperature) [5–8]. This effect is achieved by the self-induced convective heat transfer, which is “triggered” by the spinodal decomposition of the unstable liquid–liquid binary system [9]. An unambiguous assessment of the above results is complicated by the absence of primary data in [5–8].

## 2. Formulation of the problem

The purpose of this work is to study, based on of primary experimental data, the heat transfer of an aqueous solution of polypropylene glycol PPG-425 in the region of unstable states (these states arise upon pulse superheating of a solution with respect to the diffusion spinodal [10,11]) and to find the temporary conditions for the “switching-on” the convective mechanism of heat transfer, which are caused by relaxation processes. It is necessary to solve the following tasks: selection and, if necessary, improvement of the technique for studying short-lived states of liquid solutions with the possibility of relative measurements when the experimental parameter is changed; sample preparation and short-term measurement; comparison of heat transfer in samples with different concentrations including pure components; determination of the characteristic signs of the onset of micro-phase separation, spinodal decomposition and convection as the most natural relaxation processes in the studied temperature and concentration ranges.

## 3. Experimental

The research technique consists in creating short-term isothermal conditions for a pulse-heated wire probe in a substance and recording the heat flux through the probe surface [12–14]. The method is convenient for comparing the thermal properties of samples, including the solutions with different concentrations. The uniqueness of the method lies in the fact that the measurement of thermal properties is possible not only in the region of stable states, where the life time of the system is unlimited, but also in the region of superheated (short-lived) states, i.e. at a short-term exceeding the temperature values of the substance liquid–vapor or the solution liquid–liquid equilibrium at a given pressure.

### 3.1. Controlled pulse heating in the temperature plateau mode

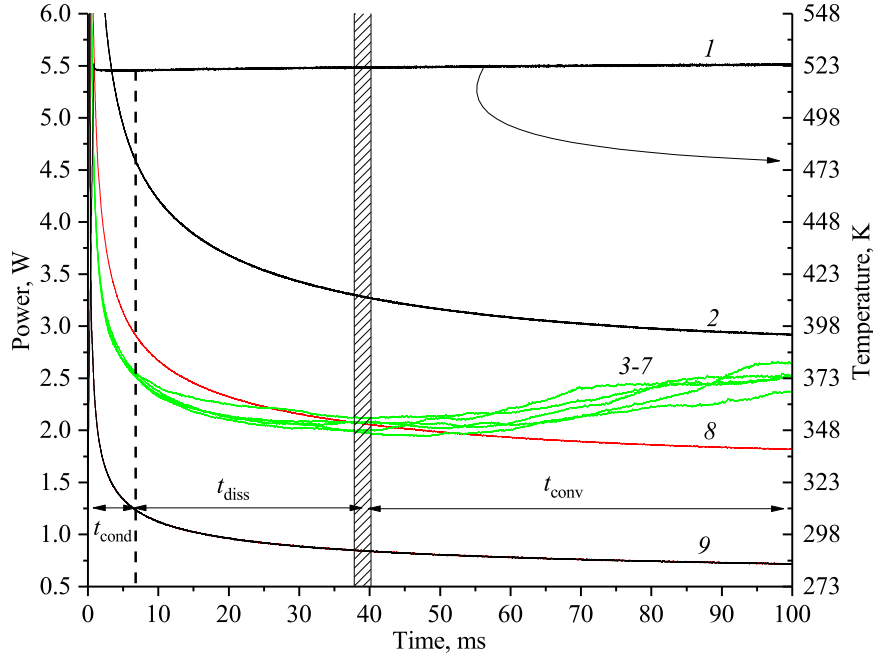
The essence of this mode is to create short-term isothermal conditions for a pulse-heated probe in a substance and to register the heat flux through the probe surface. In the course of heating, the probe temperature is increased from the initial value  $T_0$  to the selected value  $T_{st}(t_2 > t_1) = \text{const}$  for time of the order of  $t_1 = 10^{-4}$  s and is further maintained for a given time interval  $t_2 = 10^{-2}$  s. In the experiment, the values of voltage drop at the probe and standard resistor are simultaneously measured. The measured values are converted to the probe temperature  $T_{st}(t)$  and the electric power  $P(t; T_{st})$  necessary to maintain it, in figure 1. According to the measurement results, the heat transfer coefficient of the sample is calculated at a given temperature  $T_{st}$ :

$$K_T(t) = \frac{P(t)}{(T_{st}(t) - T_0)S_w}, \quad (1)$$

where  $S_w$  is the probe area.

### 3.2. Characteristics of the samples

**3.2.1. Phase diagram of PPG-425 aqueous solution** The experimental points for the liquid–liquid binodal were obtained for an aqueous solution of PPG-425 at atmospheric pressure and served as the basis for calculating the position of the spinodal, in figure 2.



**Figure 1.** Experimental curves of the method of isothermal impacts: 1—the probe temperature  $T_{st} = 523$  K; 2—the required power in water; 3–7—the required power in a 50 wt % PPG-425 aqueous solution (a series of five pulses); 8—additive value  $P(t)|_{523 \text{ K}}$  calculated for this concentration; 9—the required power in PPG-425. Probe orientation is  $45^\circ$ , the pressure is 30 MPa. Designations are as follows:  $t_{\text{cond}}$  is the conductive heat transfer interval,  $t_{\text{diss}}$  is the micro-phase separation section,  $t_{\text{conv}}$  is the convective heat transfer region.

A theoretical description of the binary system can be performed using the regular solution model. In this model, the thermodynamic potential is represented as a function of concentration and temperature:

$$F(x, T) = a(T)x^2 + \lambda x - T(x \ln(x) + (1 - x) \ln(1 - x)), \quad (2)$$

where  $x$  is the concentration of the second component,  $a(T)$  and  $\lambda$  are the temperature-dependent parameters.

The chemical potential of the solution at given concentration and temperature is a derivative of the thermodynamic potential with respect to the concentration of the second component:

$$\mu = \partial_x F(x, T) = 2a(T)x + \lambda - T(\ln(x) - \ln(1 - x)) = 2a(T)x + \lambda - T \ln\left(\frac{x}{1 - x}\right). \quad (3)$$

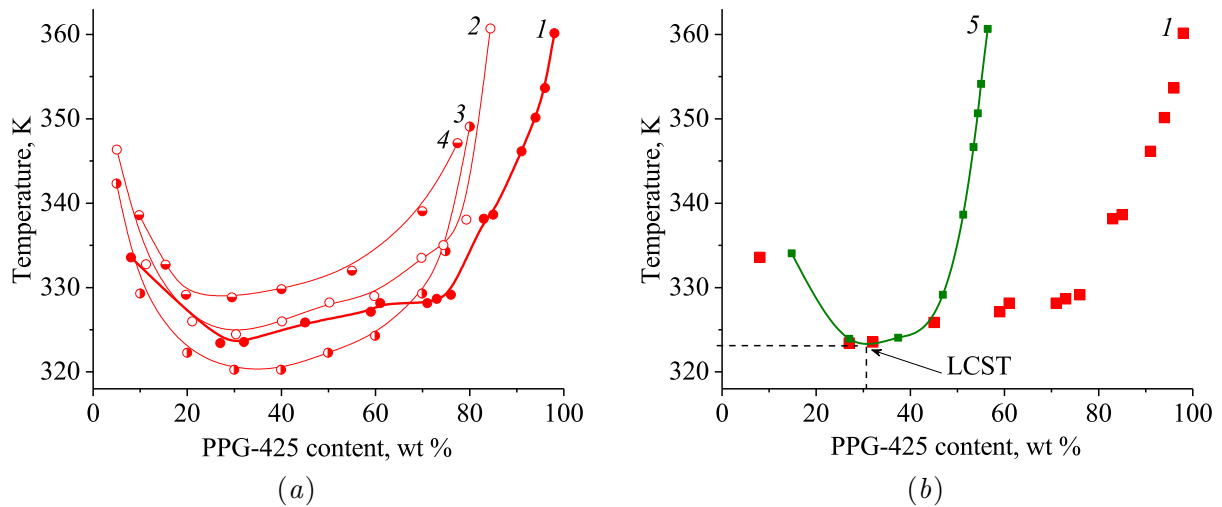
In the case of phase separation in the system, when the system is divided into regions with high and low concentration of the second component, which are two different phases, the condition for the binodal is a condition for the equal chemical potentials of these phases:

$$\mu_1 = \mu_2. \quad (4)$$

Therefore, it follows that

$$2a(T)x_1 - T \ln\left(\frac{x_1}{1 - x_1}\right) = 2a(T)x_2 - T \ln\left(\frac{x_2}{1 - x_2}\right), \quad (5)$$

$$2a(T)(x_1 - x_2) = T \ln\left(\frac{x_1}{1 - x_1}\right) - T \ln\left(\frac{x_2}{1 - x_2}\right) = T \ln\left(\frac{x_1(1 - x_2)}{x_2(1 - x_1)}\right), \quad (6)$$



**Figure 2.** The results of determination of the liquid–liquid binodal position (red dots: 1—this work; 2—[15]; 3—[16]; 4—[17]) on the plot (a); the results of determination of diffusion spinodal position (green dots: 5—this work) on the plot (b).

where  $x_1$  and  $x_2$  are the concentrations of the second component in the first and second phases, respectively.

From equation (6), it is easy to distinguish the relation between the temperature-dependent parameters of the system and the concentration:

$$\frac{2a(T)}{T} = \frac{1}{(x_1 - x_2)} \ln \left( \frac{x_1(1 - x_2)}{x_2(1 - x_1)} \right). \quad (7)$$

The condition for the spinodal transition is determined by the vanishing of the second derivative of the thermodynamic potential with respect to the concentration of the second element,

$$\partial_x^2 F(x, T) = 2a(T) - T \left( \frac{1}{x} + \frac{1}{(1 - x)} \right) = 0, \quad (8)$$

which can be represented in the following form:

$$\frac{2a(T)}{T} = \frac{1}{x(1 - x)}. \quad (9)$$

Using the concentration dependence of the  $2a(T)/T$  ratio known from equation (9), we find the equation for the spinodal  $x = x_s(T)$ :

$$x^2 - x + \frac{T}{2a(T)} = 0, \quad (10)$$

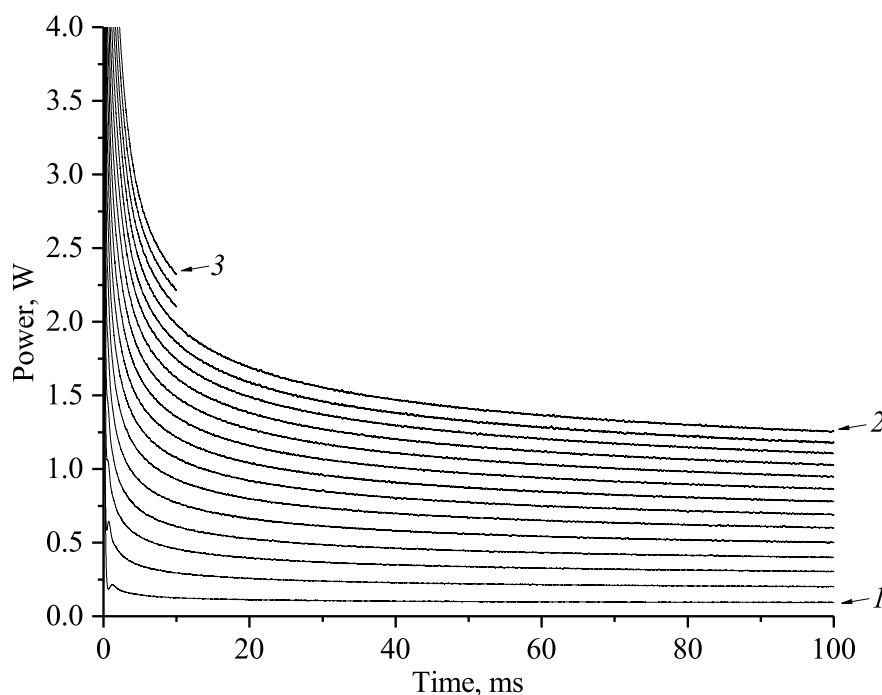
that is

$$x^2 - x + \frac{(x_1 - x_2)}{\ln \left( \frac{x_1(1 - x_2)}{x_2(1 - x_1)} \right)} = 0. \quad (11)$$

The solution to this quadratic equation has the following form:

$$x_{s\pm} = 1/2 \pm \sqrt{1/4 - \frac{(x_1 - x_2)}{\ln \left( \frac{x_1(1 - x_2)}{x_2(1 - x_1)} \right)}}. \quad (12)$$

Now, knowing the binodal positions  $x_1(T)$  and  $x_2(T)$  at temperature  $T$ , we can determine the positions  $x_{s+}$  and  $x_{s-}$  of the spinodal at a given temperature.



**Figure 3.** The values of the power amplitude in pure PPG-425 at the  $T_{st}$  values of (1) 323, (2) 648 and (3) 723 K with increments of 50 K. Pressure in the cell is 30 MPa; probe orientation is  $45^\circ$ .

**3.2.2. Samples and their preparation** The samples under investigation were prepared by mixing bidistilled water and Poly (propylene glycol), number-average molecular weight,  $M_n \sim 425$  (Sigma-Aldrich, CAS No. 25322-69-4).

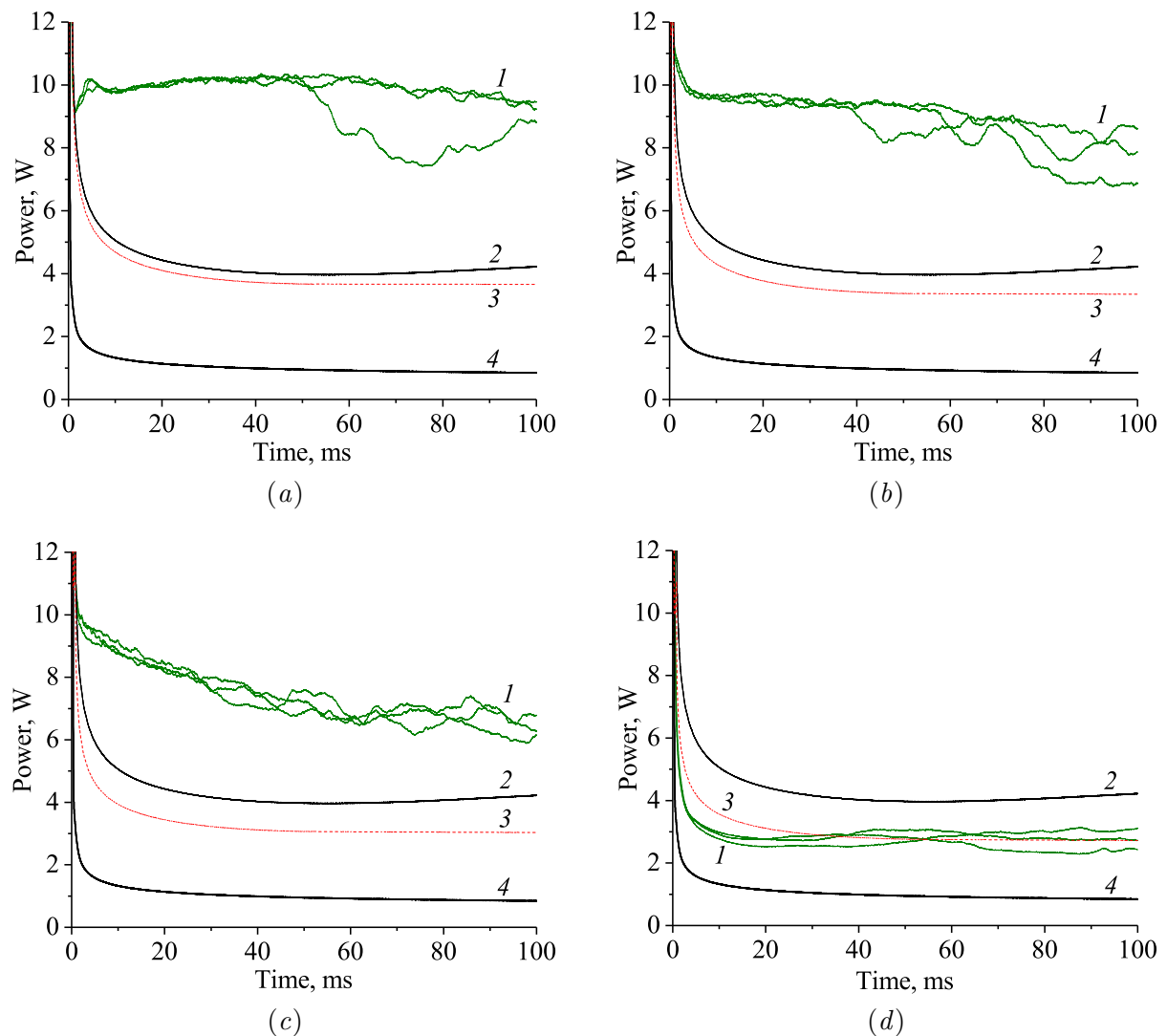
Six samples of aqueous solutions of PPG-425 with a concentration of 10, 20, 30, 40, 50 and 70 wt % were prepared. The volume of each sample was 15 mL. The concentration determination error was  $\pm 0.05$  wt %.

The samples were weighed using a Sartogsm bp 221s laboratory electronic balance of the special accuracy class (division value 0.0001 g). The components were mixed in a “Quick 218 Ultrasonic Cleaner” ultrasonic disperser.

### 3.3. Measurements

In order to exclude the boiling-up of the solutions during pulse heating, the studies were carried out at a supercritical pressure of 30 MPa. The measurements of power in time  $P(t)$  were carried out in the thermal stabilization temperature range  $T_{st} = 323\text{--}723$  K.

The measurements were carried out on a platinum probe of 20  $\mu\text{m}$  in a diameter. The initial resistance at  $T_0 = 298$  K was  $R_0 = 2.98 \Omega$ . The pulse duration of isothermal exposure was up to 100 ms. The primary data were recorded using an automated installation, which includes a probe heating circuit, a high-speed analog-to-digital converter and original software for recording primary data values in a file and calculating the corresponding  $T(t)$  and  $P(t)$  values. For each sample, at selected temperature and pressure values, from 3 to 5 pulses were recorded. If necessary, the data were averaged and smoothed. The measured values of the power of the pure components were used to construct additive values of the corresponding concentrations of the samples, which were compared with the experimental  $P(t)$  values for solutions.

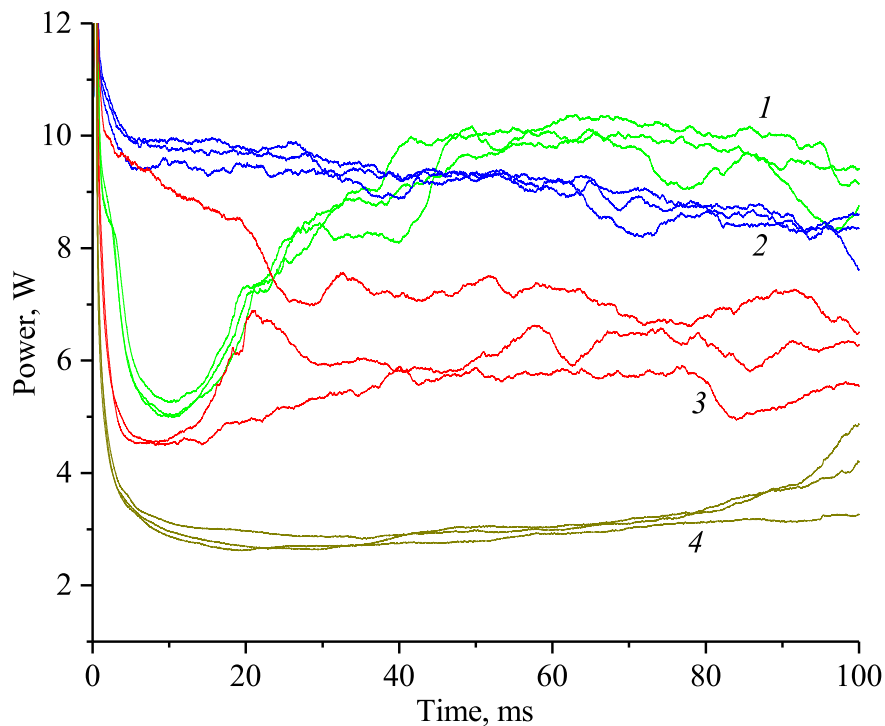


**Figure 4.** Dependence of the power required for thermal stabilization of the probe with its horizontal orientation ( $0^\circ$ ) at  $T_{st} = 573$  K: 1—series of green lines of the solution with the following oligomer content: (a) 10, (b) 20, (c) 30 and (d) 40 wt %; 2—in water; 3—the additive values (red line) calculated from lines 2 and 4 for the corresponding contents; 4—in PPG-425.

#### 4. Results

At first, we determined the position of the liquid–liquid binodal and the LCST coordinates on the temperature–concentration diagram. The position of the binodal was determined visually (turbidity method) by slow increasing the temperature in the thermostat; the concentration value served as an experimental parameter at atmospheric pressure. There was a “trembling” of points near the smooth curve and a mismatch with the data of other authors, primarily in the region of high PPG-425 concentrations, in figure 2(a). The spinodal position was estimated based on the data on the binodal obtained within the regular solution model, in figure 2(b).

Experimental data at a pressure of 30 MPa are shown in figures 3–5. The probe temperature in the thermostabilization mode was recorded at the indicated  $T_{st}$  values. The monotonicity and/or uneven nature of the curves of the heating power in the initial components and in the samples of a solution allows us to judge the signs of thermal decomposition of the oligomer



**Figure 5.** Dependence of the power required for thermal stabilization of the probe with its vertical orientation ( $90^\circ$ ) at  $T_{\text{st}} = 573$  K in solution at PPG-425 contents: (1) 10, (2) 20, (3) 30 and (4) 40 wt %.

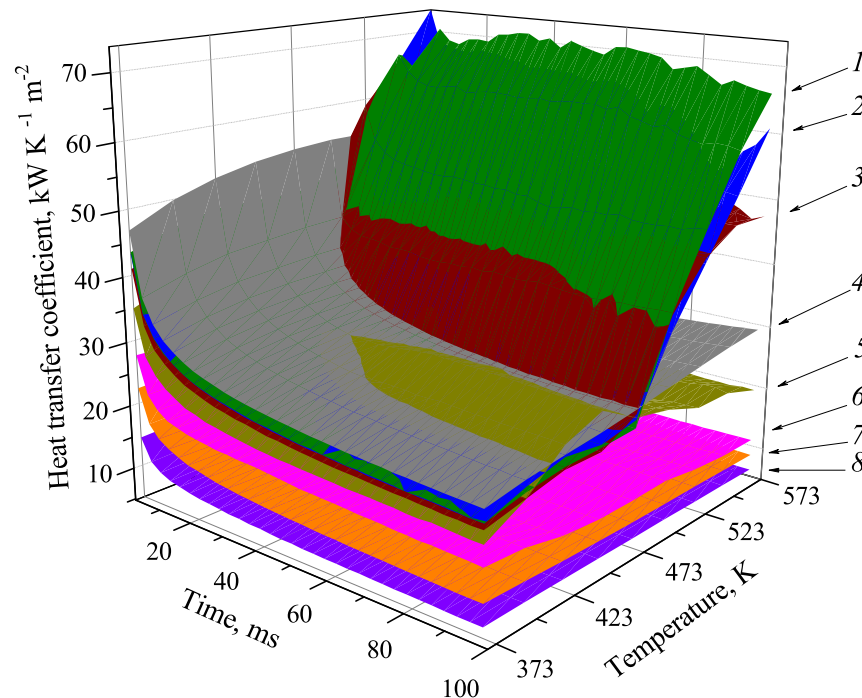
and the beginning of complex heat transfer associated with sample micro-phase separation and convection.

Short-term thermal stability of PPG-425 was studied by the method of pulse heating. Heating parameters were chosen in the following ranges: the thermostabilized pulse duration, 10–100 ms; the temperature values, 323–723 K. No signs of thermal decomposition (the presence of sharp changes in the monotonic behavior of the  $P(t)$  curves) were detected in this temperature–time range, in figure 3. The absence of signs of convection of the substance is indicated by a smooth decrease in the value of thermal stabilization power  $P(t)$ .

Experimental data on the thermal stabilization power  $P(t)$  in a sample with 10 wt % PPG-425 at  $T_{\text{st}} = 573$  K allow estimating the energy of pulse on the level of 1 J for a pulse of 100 ms duration, in figure 4(a). The fact of exceeding the pulse power not only relative to the additive value for this concentration, but also to pure water may indicate the implementation of the spinodal decomposition comprising the most natural relaxation process across the studied temperature and concentration ranges of the phase diagram. The time-confined effect of changing the direction of the response curve (see, as an example, the characteristic minimum on the green curves, figure 5) is obviously caused by the action of this process. A comparison of the data in figures 4 and 5 indicates that a change in the orientation of the probe in space at  $T_{\text{st}} = 573$  K can cause a delay in the onset of spinodal decomposition for an aqueous solution of PPG-425; in this case the delay duration is 30–50 ms.

Calculated values of the heat transfer coefficient for the solutions according to the primary data for six concentrations and two initial components is shown in figure 6. The data were plotted for a time range from 1 to 100 ms and a temperature range from 373 to 573 K in





**Figure 6.** Calculated coefficient of instant heat transfer from the probe to a PPG-425 aqueous solution according to primary data; PPG-425 content serves as an experimental parameter: (1) 10, (2) 20, (3) 30, (4) 0, (5) 40, (6) 50, (7) 70 and (8) 100 wt %. The pressure is 30 MPa.

increments of 25 K. There is a typical pattern of a monotonic change in the heat conduction of pure components and the 50 wt % sample. When the PPG-425 content in water is 40 wt %, the value of heat transfer has a maximum at  $T_{st} = 423\text{--}448\text{ K}$  that is associated with the enhanced heat exchange. A section of the beginning of heat exchange intensification is observed at  $T_{st} = 473\text{--}498\text{ K}$  and PPG-425 concentrations of 10–30 wt %. Subsequently, when temperature is raised to  $T_{st} = 573\text{ K}$ , a sharp increase in the power consumed is observed. It can be seen that  $K_T(t)$  values with a concentration of 10–30 wt % exceed the corresponding values for water by 1.5–2 times. A similar result was obtained at spinodal decomposition of an aqueous solution of triethylamine [5,6].

## 5. Conclusion

The experiments revealed the possibility of crossing the LCST line and the diffusion spinodal of an aqueous solution. For solutions with a PPG-425 content of more than 50 wt %, the duration of the section of conductive heat exchange during pulse heating  $\approx (20\text{--}30)\text{ ms}$  was determined, which is much less than the duration of the undisturbed heat exchange for pure components (more than 100 ms); their heat conduction values were less than the corresponding additive values of the solution. At a PPG-425 concentration of 40 wt %, there is a maximum associated with various types of relaxation processes such as micro-phase separation and “damped” convection of the sample that is likely to be due to the return to the region of stable states above the expected UCST line [18]. At a concentration of 10–30 wt %, the heat transfer values in the entire temperature range exceeds the corresponding additive values of the solution, and at temperatures of 473–573 K it significantly exceeds the corresponding values for water. This phenomenon can be of practical importance in the manufacture of miniaturized cooling systems,

including for improving heat exchange in micro-channels. A comparison of the concentration region with signs of heat exchange intensification and the inner region of the spinodal indicates a correlation of the latter and suggests the implementation of spinodal decomposition.

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